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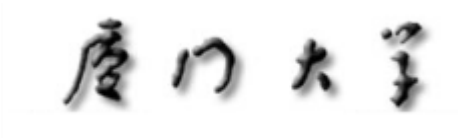

硕 士 学 位 论 文

闽南沿海大气 PM_{10} 中有机酸的分布与来源研究

Study on sources and distributions of organic acids in PM_{10} in the coastal regions of southern Fujian

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目 录

Contents

摘要

有机酸是大气气溶胶中重要的一类极性有机化合物，来源于机动车尾气、化石燃料和生物质燃烧及烹饪油烟等，不饱和脂肪酸和芳香烃（如苯、甲苯、萘）的光化学氧化以及高等植物及微生物等也有贡献。大气气溶胶中有机酸对全球的气候环境（如辐射平衡、降雨）和人类健康具有重要的影响。闽南沿海（此文定义包括厦门、金门、漳州和泉州部分沿海区域）是中国沿海经济较为发达的区域之一，也是海峡西岸经济区建设的主要引擎之一。近年来随着大厦门城市化和经济的快速发展，空气质量呈现逐年下降的趋势（首要污染物为可吸入颗粒物PM_{10}），而有机酸是 PM_{10} 中受人类活动影响明显的重要有机组成之一，有必要对其时空分布和来源进行研究。

在闽南沿海设置 10 个大气 PM_{10} 采样点，于 2010 年 4 月至 2011 年 3 月分月采集昼夜样品（3 次/月），并对样品中 15 种有机酸进行定性和定量分析，分别对其组成特征、季节变化特征、昼夜变化特征及空间变异特征等进行讨论，并结合可能的排放源，对机动车尾气、烹饪油烟、生物质燃烧、土壤及路面尘等进行有机酸源谱特征分析，以期对闽南沿海 PM_{10} 中有机酸的来源进行定性和定量分析，进一步探讨人类活动对空气质量的影响。通过以上研究，得到以下结果：

1、闽南沿海大气 PM_{10} 中有机酸以乙二酸（di-C_2）浓度为最高，其次为十六烷酸（$C_{16:0}$），十八烷酸（$C_{18:0}$）或丙二酸（di-C_3），其中夏季邻苯二甲酸（Ph）的浓度要高于 $C_{18:0}$；受季风和排放源的影响，有机酸总浓度季节变化表现为春冬高夏秋低，而 di-C_3 和 Ph 表现为夏季高，区别于其它有机酸春冬高的特点。

2、不同季节有机酸总浓度普遍表现为昼高夜低，但差异并不显著，说明存在光化学转化的影响；厦门地区一元酸均呈现昼高夜低趋势，但二元羧酸中的壬二酸表现为昼低夜高的特征，其余二元羧酸大部分表现为昼高夜低的特征；金门地区一元酸和二元酸均表现为昼高夜低的特征。

3、受本地排放源强度的影响，有机酸总浓度在厦门和泉州站点高于金门站点，其中金门烈屿国中为金门地区浓度最高点，厦大海洋楼和晋江安海成功小学两采样点浓度居高；与其它地区报道的结果相比，闽南沿海大气 PM_{10} 中有机酸总浓度污染水平较低，仅高于海洋和偏远地区，而二元羧酸的含量远低于中国内

陆城市。

4、源谱分析显示，$C_{16:0}$ 和 $C_{18:0}$ 可指示土壤和地面尘，di-C_9 可指示木材燃烧，$C_{16:0}$ 可指示生物质燃烧，Ph 可指示机动车尾气，亚油酸（$C_{18:2}$）和油酸（$C_{18:1}$）可指示烹饪油烟；来源特征比值（di-C_3/di-C_4、di-C_6/di-C_9 和 Ph/di-C_9）及多元统计分析（PCA 和多元线性回归）分析显示，闽南沿海大气 PM_{10} 中有机酸来自机动车尾气和烹饪油烟占 29.13 %以上，而春季受耕种和外来尘输入的影响显示土壤/路面尘的贡献达 21.24 %，夏季光化学转化输入贡献达 21.01 %；不同季节未知源类的贡献约占一半，表明大气 PM_{10} 中有机酸来源较为复杂。

关键词：有机酸；季节变化；昼夜变化；源谱分布；污染来源

Abstract

Organic acids are an important kind of polar organic compounds in the atmospheric aerosols. The organic acids in atmospheric aerosols may result from direct emissions (like vehicle exhaust, combusion processes of fossil and biomass, cooking) and secondary photochemical reactions (like oxidative degradation of unsaturated fatty acids and aromatic hydrocarbons). In addition, biogenic sources of organic acids including higher plants and microorganisms emissions also contribute to the compounds in PM_{10}. They have been extensively studied mainly because they play an important potential role in affecting the global climate and human health. they may have direct and indirect effects on the earth's radiation balance by scattering incoming solar radiation, and increase the acidity of rainfall. The Great Xiamen Bay (including Xiamen, Kinmen, part of Zhangzhou and Quanzhou) is an important engine of Western Taiwai Straits Economic Zone. With the rapid development of urbanizalation and economy, large amount of air pollutants emitted due to energy consumption have deteriorated the atmospheric environment (PM_{10} as the primary air pollutant). Thus, it is important to investigate the temporal and spatial variations and source contributions of organic acids in PM_{10} due to the anthropogenic activity in the coastal regions of southern Fujian.

In this study, the PM_{10} samples were collected on quartz filters with high-volume air samplers in the coastal regions of southern Fujian. The sampling sites include Xiamen (two sites), Quanzhou (three sites) and Kinmen (five sites). The PM_{10} samples were collected three times a month from April 2010 to February 2011, conducted daytime and nighttime every time. Fifteen kinds of organic acids were detected for PM_{10} samples, including saturated and unsaturated monocarboxylic acids ($C_{16:0}$, $C_{18:0}$, $C_{18:2}$, $C_{18:1}$ and t-$C_{18:1}$), dicarboxylic acids in the range of di-C_2～di-C_{10} and aromatic acids (Ph). The characteristics of compositions, seasonal variations, diurnal variations, spatial variations and so on have been discussed. The simulated source samples, including vehicle exhaust, cooking fumes, biomass burning, soil and road dust, have been collected and analyzed. So as to analyze the sources of organic

acid in PM_{10} in the coastal regions of southern Fujian by applying both qualitative and quantitative methods, and further discuss the influence of human activities to the air quality. Depending on all above studies, we can obtain the results as follows:

1. Oxalic acid (di-C_2) was found as the most abundant species in PM_{10} in the coastal regions of southern Fujian, followed by palmitic acid ($C_{16:0}$), stearic acid ($C_{18:0}$) or malonic acid (di-C_3), but the abundance of phthalic acid (Ph) was highter than $C_{18:0}$ in summer. The seasonal variations were influenced by monsoon and emission sources, the concentrations of total organic acids were higher in winter and spring than that in summer and autumn. The concentrations of monocarboxylic acids, dicarboxylic acids were also higher in winter and spring, except for some species like di-C_3 and Ph.

2. The concentrations of total organic acids were generally higher during the day in four seasons, indicating that most organic acids were photochemical products. In comparison with di-C_9, the concentrations of monocarboxylic acids and most carboxylic acids tended to be high in the daytime and low at night in Xiamen area. The trends of diurnal variations of monocarboxylic and carboxylic acids were more consistent in Kinmen area, which showed the concentrations were higher during the day.

3. Spatial variations of oganic diacids were characterized by higher concentrations in the Xiamen and Quanzhou area and lower concentrations in the Kinmen area, and the highest concentrations were observed in the traffic, residential, industrial or mixed area during winter and spring. However the pollution levels of organic acids in PM_{10} in the coastal regions of southern Fujian were generally lower.

4. The analytical results of source spectrum indicated that soil and road dust, wood burning, biomass burning, vehicle exhaust and cooking fumes were characterized by $C_{16:0}$ and $C_{18:0}$, di-C_9, $C_{16:0}$, Ph, $C_{18:2}$ and $C_{18:1}$ respectively. Utilizing those source spectrums analytical results, based on the ratios of malonate acid to succinate acid (di-C_3/di-C_4), which wre used to distinguish primary sources from secondary sources of diacids, it could be found that secondary sources contribute more than primary ones in the summer. The ratios of adipic acid to azelaic acid and phthalic acid to azelaic